An Assessment of Benzo(a)pyrene Air Emissions in the Great Lakes Region

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ABSTRACT

Benzo(a)pyrene is a persistent toxic substance whose presence in the environment is of concern due to impacts on wildlife and human health. In 1997, it was listed as one of twelve "Level I Compounds" under the U.S.-Canada Binational Toxics Strategy. The two nations have committed to pursuing benzo(a)pyrene emission reduction strategies and tracking the progress of these efforts. Emissions inventories are valuable ways of identifying high-emitting sectors, determining the relative benefit of various emission reduction strategies, and for tracking trends. The eight U.S Great Lakes states and the Canadian province of Ontario have been collaborating on a regional toxic air emissions inventory for the past 15 years. Following the publication of the 2002 inventory, these states and province conducted a specific assessment of the benzo(a)pyrene emissions inventory, including its coverage, estimation methods, available emission

factors, errors and inconsistencies. Updates were made to the data to produce a regional inventory with greater accuracy, consistency and comprehensiveness.

This paper details the emissions inventory assessment process, presents the revisions to the 2002 regional benzo(a)pyrene inventory, offers recommendations for correcting gaps in estimation tools for a variety of emission sources . The paper also discusses implications for both benzo(a)pyrene control strategies and future emission inventory work for this and other pollutants.

BACKGROUND

Benzo(a)pyrene

Benzo(a)pyrene is a persistent toxic substance that has raised concerns for human and wildlife health due to its presence at high concentrations in the waters and sediments of the Great Lakes – St. Lawrence River system. It is one of twelve Level I Substances to have been identified and targeted for reduction efforts under the Great Lakes Binational Toxics Strategy. As a member of a group of chemicals known as polycyclic aromatic hydrocarbons (PAHs), benzo(a)pyrene is comprised of five joined benzene rings. As with other PAHs, it is emitted to the environment primarily from combustion processes. Although less persistent than many halogenated toxic substances, benzo(a)pyrene persists long enough in the atmosphere to be transported efficiently on a regional scale (e.g., 1000 km) and once deposited to water bodies and sediments, can be retained in those compartments for a period of several years before being degraded. Because of its moderate persistence, there is hope that emission reduction efforts will result in lowering environmental levels within a relatively short timeframe.

Benzo(a)pyrene is listed as a probable human carcinogen (category 2B) by the U.S. EPA, based largely on data from animal studies.[1] Evidence of cancer in humans is substantial for mixtures of PAHs, but adequate work has not been done to establish cancer risks for individual PAH compounds such as benzo(a)pyrene.[1,2] Information on the human toxicity of benzo(a)pyrene following oral exposure is not sufficient to derive a reference dose (RfD).[2] While not the most abundant PAH in most emission streams or environmental samples, benzo(a)pyrene is generally regarded as a principal contributor to the overall environmental and human health risk from PAH contamination. For example, applying a set of toxic equivalency factors (TEFs), Petry et al. estimated that the contribution of benzo(a)pyrene to the total PAH toxicity in 6 occupational and 2 ambient air environments ranged from 27-67%.[3,4]

A comparative risk assessment using various methodologies showed that exposure through consumption of plant and animal products are the primary human exposure route for benzo(a)pyrene, with inhalation contributing significantly to cancer risk in several cases where relatively high cancer slope factors for inhalation were used.[4] Depending on the methodology used, cancer risk for the general population from benzo(a)pyrene and/or total PAH compounds may be as high as one in ten thousand.[4, 5]

Benzo(a)pyrene in the Great Lakes Environment

Benzo(a)pyrene concentrations have been well documented in the air, water and sediments of the Great Lakes basin. Being among the chemicals monitored by the Integrated Atmospheric Deposition Network (IADN), the record of benzo(a)pyrene within the region's air and precipitation is quite good. The IADN has collected air samples every 12 days and 28-day precipitation samples at as many as 15 sites since 1990. Results from an urban monitoring station in Chicago suggest a very strong urban-rural gradient, with air and precipitation concentrations at this station being 1-2 orders of magnitude higher than at other IADN stations. A significant long-term trend is not apparent in the IADN results for benzo(a)pyrene, with the exception of decreasing trend in precipitation from Chicago.[6, 7] Atmospheric benzo(a)pyrene loadings (wet and dry deposition) to the Great Lakes from 1992-2000 were calculated by IADN to range from roughly 5 to 25 ng/m^2-day, with deposition to Lakes Erie and Ontario generally being higher than for the other lakes and Lake Superior receiving the lowest deposition rate.[8]

Being a chemical of moderately-high environmental persistence and moderately hydrophobic, benzo(a)pyrene may cause health impairments or ecological harm due to their partitioning to sediments and subsequent accumulation in the food chain. Sediment concentrations within the Great Lakes region are fairly well characterized, although many measurements are within highly impacted area. In a sediment survey (published in 2005) of 38 lakes across the U.S., it was found that concentrations of PAH were increasing in nearly all lakes over time.[9] It was also found that of those lakes in densely populated urban areas, approximately 50% exceeded the probable effect concentration (PEC) for benzo(a)pyrene (1450 ng/g).[10] It is clear that many locations around the region have concentrations near or greater than this level. [9, 11-18] In addition, many more areas have concentrations greater than the threshold effect concentration (TEC) of 150 ng/g.[10]

In addition to sediments, soils are also an important reservoir for benzo(a)pyrene. A worldwide survey of soil concentrations in temperate regions showed benzo(a)pyrene concentrations ranging from 2 to 6461 ng/g, with urban soil concentrations being generally higher than forested, which were slightly higher than grasslands and arable soils.[19] A set of paired sediment and nearby soil samples in upstate New York showed relatively higher concentrations in soil samples compared to sediment.[20]

The Great Lakes Regional Toxic Air Emissions Inventory

The Great Lakes Regional Toxic Air Emissions Inventory is a unique program, developed from the ground up by the eight Great Lakes states and the Province of Ontario during the two decades since the signing if the Great Lakes Toxic Substance Control Agreement of 1986. This effort has included the development and refinement of an agreed-upon regional Protocol, design and implementation of project software, creation of an internet data access tool, and production of triennial regional inventories for 1993, 1996, 1999 and 2002, with intervening updates for 1997, 1998 and 2001 data years.

A Steering Committee, comprised of one or several members from each of the participating state or provincial air quality control agencies, leads development of inventories and serves as experts for quality assurance of state, provincial and national data. Each participating jurisdiction benefits through the Committee's shared expertise on software and database tools for state and provincial inventory development, capacity building and shared data dissemination tools. To date, the project has produced of several, continually improving regional inventories and has promoted their incorporation into regional scientific initiatives and policy decisions. The project's Centralized Air emissions Repository On-Line (CAROL), provides user-friendly online access to toxic air emissions data. There remain numerous challenges that must be addressed to achieve the goals of the project.

The objective of the Great Lakes Regional Toxic Air Emissions Inventory is to present researchers, policymakers and other interested stakeholders with detailed, accurate, consistent and up-to-date regional data on the sources and emission levels of toxic air pollutants for the Great Lakes region. These data provide the foundation for a better understanding of the patterns and impacts of multi-media human and wildlife exposures and provide information supporting the reduction of adverse affects to the environment and human health. In 2005, U.S. EPA and Environment Canada identified inventory improvement as one of three critical management actions needed to address the benzo(a)pyrene goals under the Great Lakes Binational Toxics Strategy.[21] The assessment presented here is an important step toward fulfilling that need.

METHODOLOGY

The benzo(a)pyrene emission assessment was conducted to improve the comprehensiveness, accuracy and consistency of the emissions inventory data in the Great Lakes region. The 2002 version of the Great Lakes regional toxic air emissions inventory was used as the basis for analysis. First, several quality assurance checks were run on the pre-existing data to identify abnormalities in the data for individual jurisdictions, source types, and industrial facilities within the region. Where errors or discrepancies were uncovered, corrections were identified and implemented. Where additional, unreported sources were identified, emission estimates were generated and included in the inventory.

Second, benzo(a)pyrene emissions for each source classification code (SCC) in the 2002 inventory were compared to those with available emission factors from U.S. EPA’s Factor Information Retrieval (FIRE) database, the 2002 U.S. EPA’s National Emissions Inventory (NEI) documentation, and other available sources. A record was made of SCCs that were associated benzo(a)pyrene emissions in the inventory but emission factors for which are not available in FIRE or NEI. Participating states and province were asked to examine and justify the inclusion of emissions from such SCCs. Similarly, cases where emission factors exist but where an individual state or province did not report benzo(a)pyrene emissions were also recorded and participating states/province were asked to either include these sources or justify their exclusion.

Third, a small set of source categories (SCCs) were identified for closer attention. This set of SCCs was recognized as major potential contributors to regional benzo(a)pyrene emissions but significant variability in the presence and magnitude of emission estimates were observed. The Steering Committee examined these SCCs and developed a consensus on estimation methodology and use of appropriate emission factors. Among the source categories that were closely examined are residential wood burning, coke ovens, metal production, open burning, crematories, and mobile sources. Observations regarding each of these sources are described in the Conclusions section of this paper.

The modifications to the regional benzo(a)pyrene emissions will be included in the Centralized Air emission Repository On-Line (CAROL), web-based data storage and retrieval tool maintained by the regional emissions inventory project, and made available as a downloadable database through the project website, www.glc.org/GLAD.

ORIGINAL 2002 DATA

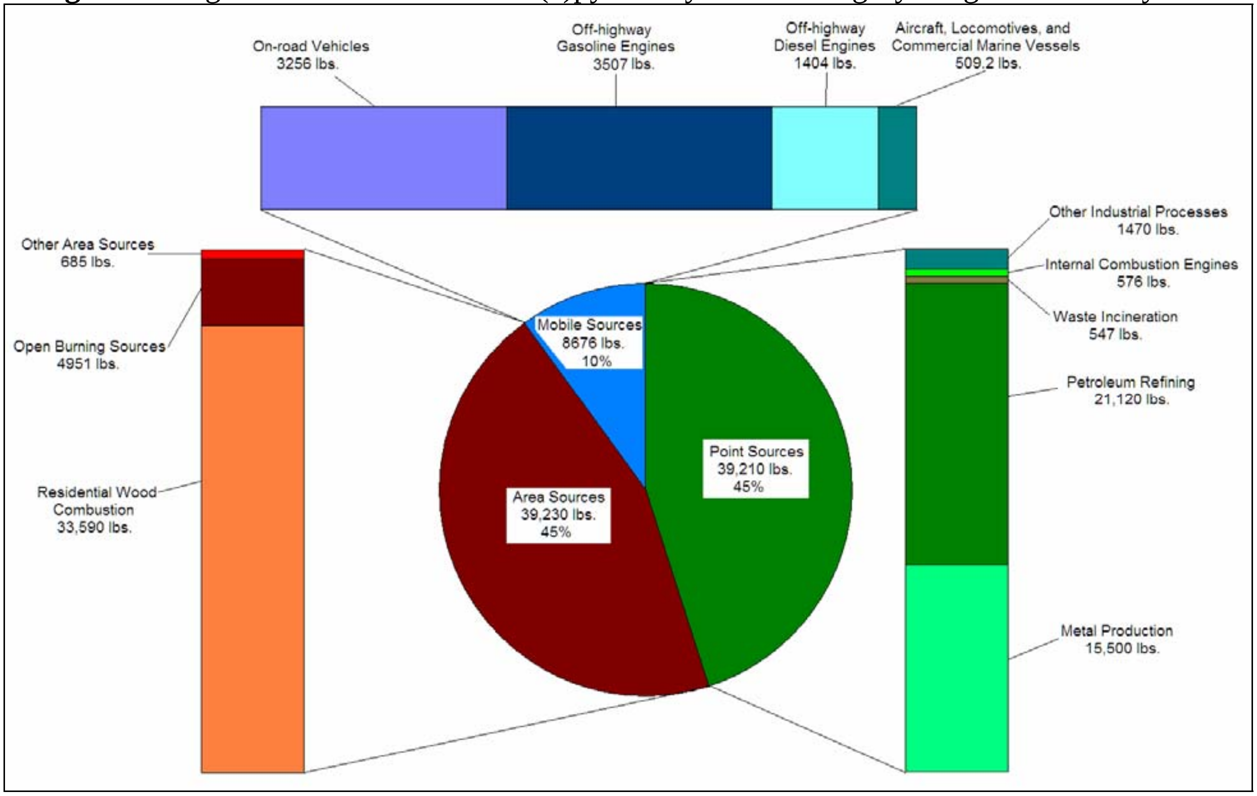
In all, the original 2002 regional inventory included 87,120 pounds of benzo(a)pyrene emissions. Total emissions for individual states ranged over nearly a factor of eight. Almost equal amounts of emissions were estimated for point and area sources, which together comprised 90% of the total emissions. Emissions from on-road and non-road mobile sources made up the remaining 10% of emissions. The total original 2002 emission estimates classified by source type and by state or province are shown in Table .

Table 1. Original 2002 regional benzo(a)pyrene emission estimates (lbs.) by source type and state/province.

Jurisdiction	Area	Point	Mobile	Non-road	Total
Illinois	1,151	3,414	354.3	218.1	**5,137**
Indiana	1,535	5,048	250.2	144.5	**6,977**
Michigan	1,152	7,228	390.7	391.5	**9,163**
Minnesota	4,555	100.3	0	199.9	**4,855**
New York	20,810	250.5	1,163	230.8	**22,460**
Ohio	1,483	15,070	373.9	3606	**20,530**
Ontario	3,853	6,162	233.4	149.4	**10,400**
Pennsylvania	2,162	1,921	303.2	267.9	**4,654**
Wisconsin	2,523	20	187.4	213.2	**2,944**
Total	**39,230**	**39,210**	**3,256**	**5,422**	**87,120**

While emission estimates were made for 697 SCCs, the highest ten of these accounted for nearly 86% of the total emissions. The 400 SCCs with the lowest estimated emissions accounted for less than 0.5% of the total emissions. Among the top categories in the original data, both point sources (fluidized catalytic cracker units, steel production, coke processing, etc.) and area sources (wood fireplaces, wood stoves, open burning, etc.) are well represented. The largest emitting categories among on-road and non-road mobile sources were outboard engine boats and snowmobiles, with estimates of 380 lbs (0.44% of the total inventory) and 231 lbs (0.27% of the total inventory), respectively. The emissions by source category are shown in **Error! Reference source not found.**.

Figure 1: Regional emissions of benzo(a)pyrene by source category: original inventory data



REVISED 2002 DATA

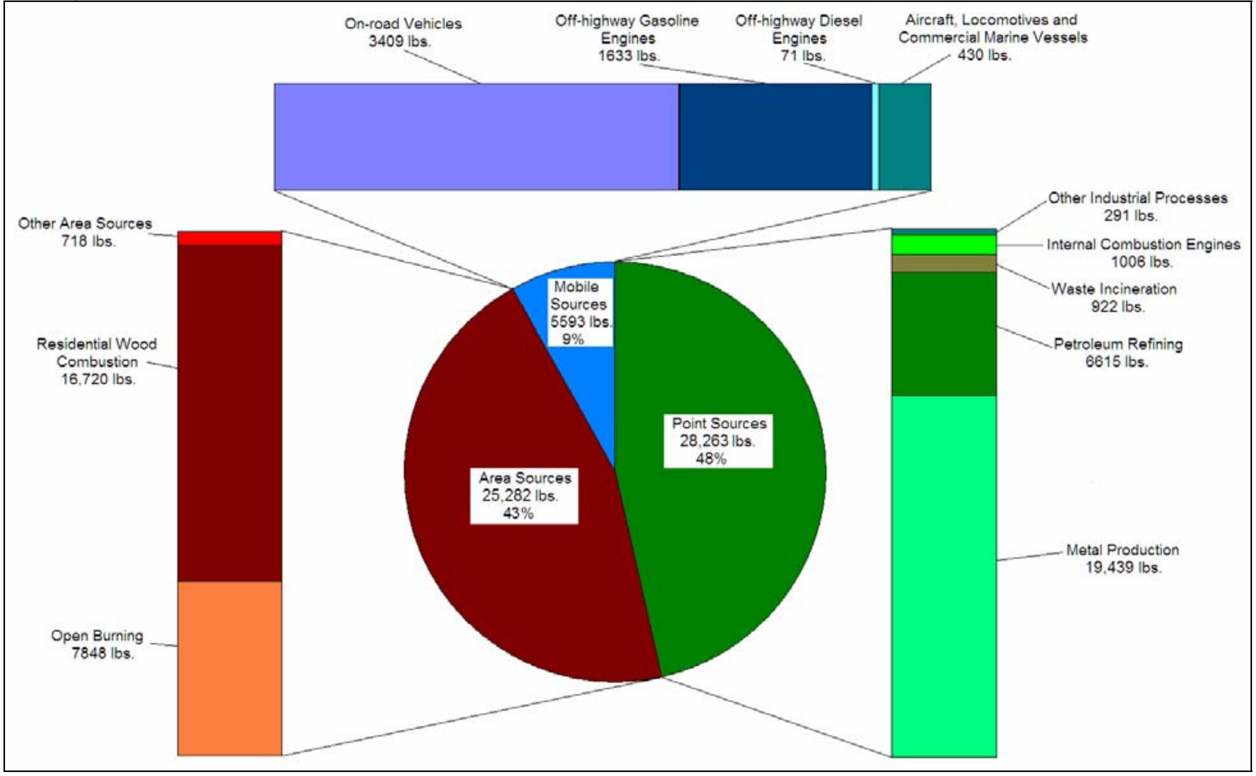
The revised inventory included a total of 59,087 pounds of benzo(a)pyrene emissions. Area and point sources contributed similar magnitudes on a regional basis, accounting for 43% and 48% of the total emissions, respectively. Mobile sources contributed the remaining 9% of regional emissions. The total revised 2002 emission estimates classified by source type and by state or province are shown in Table 2.

Table 2. Revised 2002 regional benzo(a)pyrene emission estimates (lbs.) by source type and state/province.

Jurisdiction	Area	Point	Mobile	Non-road	Total
Illinois	1,166	3,416	354	219	**5,155**
Indiana	1,535	1,802	250	146	**3,733**
Michigan	3,213	7,231	391	394	**11,229**
Minnesota	3,294	100	153	202	**3,748**
New York	4,226	6,416	1,163	231	**12,036**
Ohio	1,483	1,197	374	307	**3,361**
Ontario	4,996	6,162	233	151	**11,542**
Pennsylvania	2,162	1,919	303	269	**4,653**
Wisconsin	3,207	20.48	187	215	**3,629**
Total	**25,282**	**28,263**	**3,408**	**2,134**	**59,087**

Point sources contributed a total of 28,263 pounds of benzo(a)pyrene emissions. As shown in Figure 2, the most prominent point source category in the final inventory is metal production, which contributed 33% of the total regional emissions and 69% of the point source emissions. Petroleum refineries contributed 11% of the regional total.

Figure 2: Regional emissions of benzo(a)pyrene by source category: revised inventory data



Waste disposal, waste incineration and internal combustion engines each contributed 1-3% to the regional total. All other point source categories were relatively insignificant, combining for less than 0.5% of the total emissions. Point source emissions varied considerably among the states and Ontario, with total point source emissions ranging from 20 pounds to more than 7,000 pounds. Reasons for this difference include the variability of facility locations (some states/province having a higher density of large emitters), differences in how inventories are compiled (including varying classifications of certain source types among point and area sources) and differences in reporting thresholds.

The total benzo(a)pyrene emissions from area sources in the revised 2002 inventory are 25,282 pounds. Residential wood combustion was the most significant area source category, contributing 28% of the total regional emissions. Open burning sources, including burning of household waste, forest fire and prescribed burning, accounted for 13% of the regional total. Among other significant are sources were commercial cooking and “accidental releases” (in this case a scrap tire fire in Pennsylvania), each contributing more than 300 pounds.

Mobile sources contributed a total of 5,593 pounds to the regional benzo(a)pyrene inventory. On-road mobile sources contributed more than 60% of that amount, although only 5.4% of the total regional emissions. 2-stroke gasoline engines were by far the largest contributor of off-highway vehicles and engines. Aircraft, locomotives and commercial marine vessels contributed a combines 430 pounds, or 0.7% of the total regional emissions. Within both on-road and off-road mobile sources, gasoline engines contributed far more emissions than diesel engines.

SUMMARY OF MODIFICATIONS

The assessment and modifications to the data resulted in an overall decrease of 32% of the original estimate of regional benzo(a)pyrene emissions. This change is due to a combination of decreases and increases to estimated values from a wide variety of source categories within each jurisdiction. Beyond the significance of the substantially decreased total emission estimate, the assessment resulted in important improvements in the consistency and comprehensiveness of the regional benzo(a)pyrene inventory. In spite of these improvements, the assessment also revealed several areas where uncertainties and inconsistencies remain. These will be discussed further in the Conclusions section below.

Metal production, originally among the several highest categories, saw an increase of about 25% from the original estimate, becoming the largest source category in the final emissions inventory. This increase in this category was due largely to the inclusion of additional aluminum production sources. In contrast, petroleum refining, also among the highest categories in the original inventory, saw a reduction of nearly 70% from the original estimate. This was due to updating the emission factors and control efficiencies used for fluidized catalytic cracking units (FCCUs) based on information from several sources. This category remains a substantial contributor in the final inventory, contributing about 11% of the total emission estimate.

Among other point source processes, waste incineration increased by nearly 70% of its emissions to over 900 pounds, while internal combustion engine also saw a significant increase of about 75% of its emissions, raising the regional emissions from this category to approximately 1000 pounds.

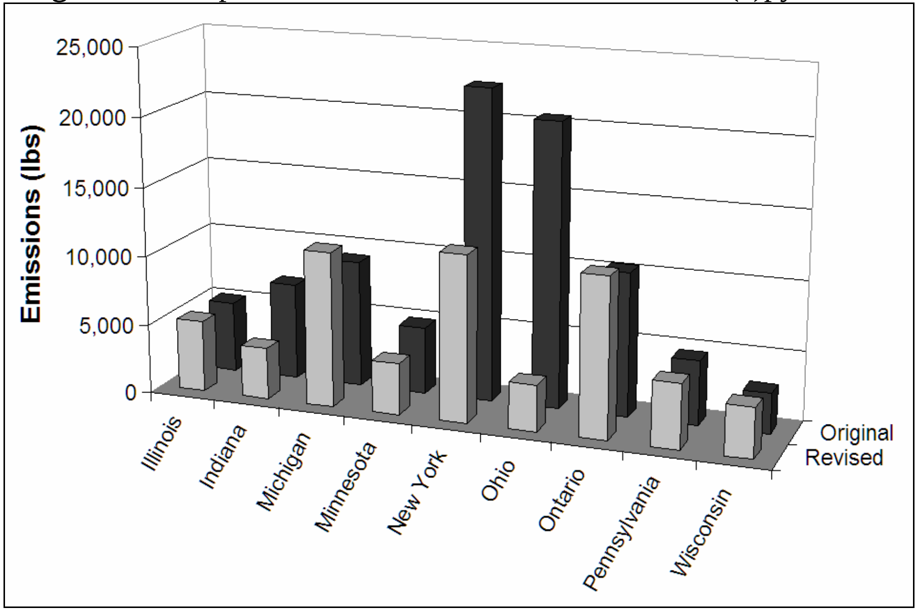
Residential wood combustion was the largest source category in the original inventory and despite an overall reduction of about 50% of emissions in this source category, it remained the second highest category in the final inventory. Reductions in this category were due largely to a substantial decrease in the estimate from New York, which was offset to some degree by the inclusion of emissions data for this category for Pennsylvania and increases in estimates from several states, including Wisconsin and Michigan.

In contrast to residential wood combustion, emissions from open burning increased substantially to 7848 lbs, representing a 59% increase over the original figure. This increase was primarily due to the inclusion of additional sources (from Michigan, Minnesota, Ontario and Wisconsin) for which emission estimation was refined and updated after compilation the original inventory. Other substantial changes in area source categories included: stationary source fuel combustion, which underwent an 84% decrease of emissions to 37 lbs; and commercial cooking, which increased its emissions by more than three-fold to 333 lbs, due to the inclusion of this category by Michigan, New York, and Wisconsin.

On-road vehicle emissions increased by 5% due primarily to the inclusion of emissions from Minnesota, which were previously omitted. Non-road engine emissions decreased substantially across all categories due to corrections to significant overestimations in Ohio's data for these categories. Total regional non-road emission estimations decreased from 5,422 pounds to 2,127 pounds.

Emissions for each jurisdiction changed by more than 20% from the original estimate, with the exception of Illinois, whose emission estimate increased by less than 1% as a result of the assessment. While benzo(a)pyrene emission estimates increased for Michigan, Ontario, Pennsylvania and Wisconsin, they decreased for Indiana, Minnesota, Ohio and New York. A comparison of benzo(a)pyrene emissions for the nine participating jurisdictions before and after the assessment is shown in **Error! Reference source not found.**.

Figure 3: Comparison of emissions estimates of benzo(a)pyrene before and after the revisions



CONCLUSIONS

The revised 2002 Great Lakes regional emissions inventory shows that the categories of residential wood burning, metal production, petroleum refining and open burning contribute more than 80% of the total regional emissions. The revised estimate of total regional 2002 emissions shows about a 32% reduction from the original 2002 estimate. In many cases, changes within a certain source category or within a certain state or province were even more substantial than the change in the overall estimates. The resulting revised inventory provides the best information base to date on benzo(a)pyrene emissions in the Great Lakes region and can serve as an important tool for scientific analysis of the fate and impacts of this chemical and for state, provincial and federal policy makers to use in targeting emission reduction strategies.

Although the revised inventory represents an important step forward, many uncertainties remain in the inventory. The uncertainties that require further investigation include uncertainties in emissions from source categories that are recognized as major potential contributors but with significant variability in the presence and magnitude of emissions, uncertainties in control effectiveness, and uncertainties due to lacking or inaccurate emission factors and/or activity data. Other factors, such as differing thresholds used by the states and province in requiring facilities to report emissions, can also lead to differences among jurisdictions within the regional inventory.

Future inventory production efforts should focus on: maintaining the improvements made here in future datasets; continuing to improve consistency in estimation methodology and reference data among jurisdictions; improve emission factors, activity data and understanding of control efficiencies; and improvement or inclusion of estimation methodologies for additional source types. To verify the results of the emissions inventory, comparison of the major source categories identified in this assessment with receptor modeling results is needed. To better understand the human and environmental health risks posed by benzo(a)pyrene in the Great Lakes region, the emissions data presented here can be employed in risk assessments and modeling initiatives. Combined with an understanding of the impacts of benzo(a)pyrene emissions, this updated inventory can support an assessment of whether further emission reductions are needed to protect human and wildlife health. If such reductions are deemed important, this inventory data can provide an important tool for identifying important sources and help assess the effectiveness of certain emission reduction strategies.

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KEY WORDS

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